Preface

The CdTe family members (in particular CdZnTe) remain the substrate of choice for epitaxial growth of HgCdTe for use in high performance infrared (IR) detectors and focal plane arrays. This is the case despite advances in the use of alternate substrate technologies such as buffered GaAs and GaAs on Si; these technologies, to date, have not reproducibly demonstrated device performance comparable to the arrays made in HgCdTe grown on CdZnTe and CdTe. The quality of CdTe family materials has improved significantly over the past several years and so the quality and reproducibility of IR detectors has improved along with them. It is clear, however, that CdTe family substrates still have a significant impact on the performance of HgCdTe devices and that further research is required to reduce the effects of substrate on these devices.

Unlike silicon or gallium arsenide, it is very difficult to grow the large area single crystals of CdZnTe due to thermodynamic limitations. It has the lowest thermal conductivity among all semiconductors that makes it difficult to obtain planar solid-liquid interface, which is desirable for the growth of large area single crystals of CdZnTe. Due to its high ionicity and weak bonding, defects are easily incorporated during the growth. Also, it is well established that both the structural defects and impurity content of $Hg_{1-x}Cd_xTe$ epitaxial layers are strongly influenced by the quality of the substrates used in the epitaxial growth process. A substrate of poor structural quality will result in a poor substrate/layer interface from which defects will propagate into the epilayer.

It is known that our focal plane arrays (FPAs) are backside illuminated, with the device connected to underlying silicon multiplexer, using a matrix of indium bumps. Thus the substrate should have high IR transmission to pass the radiation on to the detector for collection. High IR transmission requires chemically and electrically homogeneous crystals free from extraneous second phase particles. This objective is one of the most difficult thermodynamic and technological problems in the growth of CdTe and related alloys. The bulk CdZnTe crystals grown from melt suffer from the inherent disadvantage of accommodating tellurium precipitates because of high growth temperature and phase diagram limitations. These tellurium (Te) precipitates condense as cadmium vacancies and Te interstitials during the cooling process, which contribute to intrinsic point defects. Although extensive efforts have been made in the area of purification of the CdZnTe crystals by using 6N pure starting materials, still the high temperature melt growth leads to impurity pick-up during the crystal growth process. This deviation in the stoichiometry, especially due to free carriers, impurities and second phase tellurium precipitates, play the major role in reducing the infrared transmission through the CdZnTe substrate material. Also they affect the device performance when used for detector applications. In this context a thorough investigation of the non-stoichiometry of the CdZnTe material is mandatory to improve the material quality. It is my endeavor in this respect to present in this thesis “optical and structural investigations of defects in CdZnTe (Zn~4%) crystals”.

The present thesis has been organized into six chapters.

Chapter 1: It presents an up to date comprehensive review of the defects in CdTe binary and CdZnTe ternary compound semiconductors. It includes an introduction to the ternary II-VI cadmium zinc telluride with potential device applications. Issues related to CdTe based substrates for infrared (IR) applications have been discussed. Growth as well as several material aspects like crystal structure, band structure, mechanical, thermal, optical and dielectric properties have been discussed in details. The chapter ends with the motivation and scope for the present thesis.

Chapter 2 : Te precipitates were identified and characterized in CdZnTe (Zn ~ 4%) crystals using various physical characterization techniques and the results are presented in Chapter 2. X-ray diffraction rocking curve measurements were carried out on a series of samples to assess the overall crystalline quality of the as grown CdZnTe crystals, in conjunction with Fourier transform infrared (FTIR) absorption spectroscopy measurements to identify the presence of Te precipitates. Further, the CdZnTe samples having Te precipitates were systematically characterized using micro-Raman imaging technique. CdZnTe wafers grown in three and six zone furnaces using quartz and/or pyrolytic boron nitride (PBN) crucibles have been subjected to micro-Raman imaging to quantify and understand the nature of Te precipitates. It is well known that for the normal phase of Te precipitates, the Raman modes appear centered around 121 (A_1), 141(E) /TO (CdTe) cm^{-1} and a weak mode around 92 (E) cm^{-1} in CdZnTe indicating the presence of trigonal lattice of Te. Using the micro-Raman maps and taking the spatial distribution of the area ratio of 121 to 141 cm^{-1} Raman modes, the size and distribution of Te precipitates were estimated. A substantial reduction in Te precipitate size and an improvement in the IR transmission in the 2.2 – 5 µm IR window was observed in the CdZnTe crystals subjected to post growth annealing under Cd+Zn vapors at 650 ^{o}C for 6 hrs. Also it is shown that the samples grown in pyrolytic boron nitride (PBN) crucibles have shown an overall improvement in the crystalline quality and reduction in the Te precipitate size as compared to the samples grown in quartz crucibles. The possible reasons for these observations have been discussed in chapter 2. The presence of Te precipitates under high pressure phase was detected by the blueshift of the Raman bands that appear at 121 (A_1) cm^{-1} for a normal Te phase, indicating that these micro-Raman maps are basically the distribution of Te precipitates in different phases. NIR microscopy imaging has been carried out to further substantiate the presence of Te precipitates under high pressure phase and that of larger Te precipitates. The significance of micro-Raman imaging lies in quantifying and demonstrating the high pressure phase of Te precipitates in CdZnTe crystals in a non-destructive way. Also it is shown that the presence of Te precipitates lead to loss of useful signal in the 2.2 – 6 µm wavelength regions and hence are "deleterious" for substrate applications of CdZnTe crystals required for the growth and fabrication of HgCdTe detectors.

<u>Chapter 3:</u> The effects of annealing and hydrogenation on the low temperature photoluminescence (PL) spectra of CdZnTe (Zn ~ 4%) crystals are reported in this chapter. It is shown that annealing at 600 ^{o}C for 12 hrs under Cd vapors has resulted in the disappearance of both C-A and DAP recombination features (attributed to singly ionized cadmium vacancy acceptors) observed in the 1.5 – 1.6 eV band edge region in the low temperature PL spectra of CdZnTe, confirming the origination of these bands from Cd vacancy defects. The presence of copper impurity has been

identified by the appearance of the 1.616 (A^oX) eV energy peak attributed to exciton bound to the neutral copper acceptor and the 1.469 eV band attributed to copper acceptor in the donor acceptor pair (DAP) recombinations. It is shown that, only annealing under Cd+Zn vapors at 650 ^oC for 6 hrs has resulted in the passivation of the 1.469 eV band and the mechanism has been explained invoking the Hume-Rothery rule. Passivation of the 1.469 eV band is significant, since CdZnTe substrate copper contamination was found to degrade HgCdTe epitaxial layer and hence the performance of HgCdTe infrared (IR) detectors. Also it shown that vacuum annealing has resulted in the introduction of a new defect band around 0.85 eV in the low temperature PL spectra of CdZnTe possibly due to the loss of Cd and/or Zn. Further, the effects of hydrogenation in passivating the defect bands observed in the low temperature PL spectra of the control CdZnTe crystals are discussed. Using micro-Raman imaging technique, it is shown that hydrogenation has resulted in the reduction in size and restoration of normal phase for Te precipitates, which otherwise were present under high pressure phase in CdZnTe crystals. It is shown that the net effect of hydrogenation is to improve the quality of CdZnTe crystals at low temperature (50 ^oC) as compared to the high Cd+Zn annealing temperature (650 ^oC) whose effect is only to reduce the size of Te precipitates. To further substantiate this an analysis of the temperature dependent resonance micro-Raman spectra recorded with 633 and 488 nm lasers has been made and it is shown that appearance of the multiple orders (up to 4 orders) of the CdTe like LO phonon modes and emergence of the ZnTe like LO phonon mode are clear indications of the improved quality of the hydrogenated CdZnTe crystals.

Chapter 4: Manifestation of Fe^{2+} and Fe^{3+} charge states of Fe in undoped CdZnTe (Zn ~ 4 %) crystals grown in quartz crucibles by asymmetrical Bridgemann method and their respective optical and magnetic behaviors have been discussed in this chapter. Fe^{2+} being optically active shows absorption around 2295 cm^{-1} in the low temperature (T = 3 K) FTIR spectra, while Fe^{3+} being magnetically active exhibits coexistence of para and ferromagnetic phases, as identified by low temperature electron spin resonance and supported independently by low temperature SQUID and AC susceptibility measurements. In the paramagnetic phase (T_C ~ 4.8 K) the inverse of ac susceptibility follows the Curie-Weiss law. In the ferromagnetic phase (T_C ~ 4.8 K) the thermal evolution of magnetization follows the well known Bloch's $T^{3/2}$ law. This is further supported by the appearance of hysteresis in the SQUID measurements at 2K below T_C. Small coercive field of 10 Oe as estimated in the hysteresis suggests that the magnetic anisotropy is very small in these systems.

Chapter 5: In this chapter, details of the indigenously developed laser beam induced current (LBIC) instrumentation have been presented. These include instrumental arrangement of the micro-mechanical system for raster scanning of defects in semicoductors and fabrication details of continuous flow liquid helium cryostat for low temperature LBIC measurements. Preliminary LBIC data recorded using this system have been shown to demonstrate the operability of the system.

Chapter 6: This chapter includes a brief write-up summarizing the results and draws the attention for the possible future work.

Appendix A: Here C++ programs for LBIC measurements are presented.

Appendix B: Here the CAD diagrams for the full cross sectional view of the liquid helium cryostat consisting of "assembly liquid helium cryostat" and "part liquid helium cryostat" are attached.